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- Applicant: DAI-ICHI KOGYO SEIYAKU CO.,
 LTD.
 55 Higashi-Kubocho Nishi-Hichijyo
 Shimogyo-ku Kyoto(JP)
- Inventor: Motogami, Kenji A-25-106 Noborimachi 2-ban Takatsuki-shi, Osaka(JP) Inventor: Mori, Shigeo 35-1 Katsura Chiyoharacho Nishikyo-ku, Kyoto(JP)
- Representative: Seaborn, George Stephen et al c/o Edward Evans & Co. Chancery House 53-64 Chancery Lane London WC2A 1SD(GB)
- son-conductive polymer electrolyte.
- ② An ion-conductive polymer electrolyte comprises an organic polymer and a soluble electrolyte salt. The organic polymer is obtained by crosslinking a compound having an average molecular weight of 1,000 to 20,000 and having a structure of the following formula ①:

$$Z = \begin{bmatrix} CH_z - CH & -0 & & & & & \\ CH_z - O - (CH_z & -CH_z - O) & & & & & \\ & & & & & & & \end{bmatrix}_{R}$$

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in which Z is a residue of a compound having at least one active hydrogen, Y is a hydrogen atom or polymerizable functional group, m is an integer of 1 to 250, n is 0 or an integer of 1 to 25, k is an integer of 1 to 12, R is an alkyl, alkenyl, aryl or alkylaryl group having 1 to 20 carbon atoms. While the compound r presented by the formula ① in which Y is a hydrogen atom may be crosslinked with a crosslinking agent such as an isocyanate compound, the compound having a structure of the formula ① in which Y is a polymerizable functional group may be crosslinked by its If.

ION-CONDUCTIVE POLYMER ELECTROLYTE

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Background of the Invention

This invention relates to an ion-conductive polymer-electrolyte.

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As an ion-conductive polymer electrolyte, there has been known following compounds. For example, an grishomou trorganic polymer electrolyte of polyethylene oxide type; an organic polymer electrolyte having a multifuncstructure prepared by a randam copolymerization of ethylene oxide portion and propylene oxide portion (Japanese Patent Publication No.249,361 of 1987); an ion-conductive polymer to be residence trolytes comprising a branched polyethylene oxide prepared by adding ethylene oxide as the side chain ent is ro to a main chain of polyethylene oxide (Japanese Patent Publication No.136,408 of 1988); a solid polymer electrolyte comprising an ethylene oxide copolymer containing anionic compound in dissolved state (Japanese Laid-Open Patent Publication No.83,249 of 1986); and an ion-conductive polymer electrolyte in Duby rioc as which a high polymer solid substance having plasticity is further constituted substantially with a brancheddesignation of a homopolymer or copolymer which is thermoplastic and has no cross linkage (Japanese Laid-Jenic S rs. 19 Open Patent Publication No. 98,480, of 1980)

However, those conventional ion-conductive polymer electrolytes have the following problems.

First, the organic polymer electrolyte of polyethylene oxide type shows a relatively good lithium-ion evilus the real conductivity in the temperature range not lower than 40°C, but the characteristic is lowered rapidly at the proper temperature range of about 25°C. Accordingly, it is very difficult that the electrolytes used for 20 various applications such as battery, electrochromic and the like.

The organic polymer electrolytes described in Japanese Patent Publication No 249:361 of 1987 and Japanese Ratent Publication No.136, 408 of 1988 do not show rapid lowering of the lithium-ion conductivity at the room temperature range of about 25 C but the lowering proceeds at a temperature of not higher than 0 °C which is considered as a practical temperature range. Therefore, a practical ion-conductivity can not be obtained. g.,

The organic polymer electrolyte described in Japanese Laid-Open Patent Publication No.83,249 of 1986 is an organic polymer prepared by a randam-copolymerization of ethylene oxide with the other monomer. The structure of the organic polymer resultantly becomes amorphous as a result by the randomcopolymerization, but the amorphous structure is not sufficient by the difference of reactivity between each

30 5 monomers so that the product quality tends to be unstable. In Japanese Laid-Open Patent Publication No.98,480 of 1980 is thermoplastic, a film formed with it is limited only to be simple and a good adhesion .St of the between the film and the electrode cannot be obtained as videnciero et a strict

The object of the present invention is to solve such problems as described above and to provide an as ion-conductive polymer electrolyte which shows an excellent ion conductivity and can be easily handled. the indicate of containing the us and the teaching of the teaching

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elusationnyling a 1 "months & significant add or a months as product become to add control and the significant and the signifi The ion-conductive polymer electrolyte according to the invention comprises an organic polymer and a soluble electrolyte salt. The organic polymer is obtained by crosslinking a compound having an average molecular weight of 1,000 to 20,000 and having a structure of the following formula 1;

services in which Z is a residue of a compound having at least one active hydrogen (hereinafter referred to as active:hydrogen_compound), Y is a hydrogen atom or polymerizable functional group, m is an integ r of 1 to 250, n is 0 or an integer of 1 to 25, k is an integer of 1 to 12, R is an alkyl, alkenyl, aryl or alkylaryl group The grant labor having 1 to 20 carbon atoms. The proposition of a

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crosslinked uith a crosslinking ag nt such as an isocyanate compound, the compound having a structure of the formula ① in which Y is a polymerizable functional group may be crosslinked by itself.

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Detailed Description of the Invention

Thus, the ion-conductive polymer electrolyte according to the invention is characterized in comprising an organic polymer prepared by crosslinking the specific compound having a structure of the formula 10 and a soluble electrolyte salt.

The compound having a structure of the formula ① wherein Y'is a hydrogen atom cambe obtained by reacting an active hydrogen compound with giveldyl ethers in the presence of a catalyst so that the molecular weight of the reaction product becomes 1,000 to 20,000; that is, m in the formula ① becomes 1

As the active hydrogen compounds, there are exemplified the following compounds; such as polyhydric alcohols, e.g., ethylene glycol, propylene glycol, 1,4-butanediol, glycerol, trimethylolpropane; pentaerythritol, alcohols, e.g., ethylene glycol, propylene glycol, 1,4-butanediol, glycerol, trimethylolpropane; pentaerythritol, alcohols, e.g., polyglycerol, and the like; amine compounds; e.g., butylamine, 2-ethylhexylamine, and the like; amine compounds; e.g., butylamine, 2-ethylhexylamine, and the like; phenolic active hydrogen pentaethylenehexamine, aniline, benzylamine, prienylenediamine and the like; phenolic active hydrogen compounds, e.g., Bisphenol A, hydroquinone, novolac and the like; copounds having different active hydrogen-containing groups in the molecule, e.g., monoethanolamine diethanolamine and the like. Among

them, polyhydric alcohols are particularly preferred: "See Additional Compounds, there are exemplified with the active hydrogen compounds, there are exemplified the following compounds; such as methyl glycidyl ether, eithyl glycidyl ether or alkyl-ralkenyl-, aryl- or glycidyl ether, alkylaryl-polyethylene glycol glycidyl ethers represented by the following formula; and a second second

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wherein R is a straight-chain alkyli such as methyl, ethyle butyl and the like; branched alkyl such as isopropyl, sec-butyl, tert-butyl and the like; alkenyl such as vinyl, allyl, 1-propenyl, 1,3-butadienyl and the like; aryl or alkylaryl such as phenyl, nonylphenyl, tolyl, benzyl, and the like and n is an integer of 1 to 25. In the above formula, n is preferably an integer of 1 to 15 and the carbon number of R is preferably 1 to 12.

The glycidyl ethers may be copolymerized with alkylene oxides such as ethylene oxide, propylene oxide and the like within the range in which the characteristics of the organic polymer are not changed.

Generally, the following catalysts may be used in the reaction of active hydrogen compounds with glycidyl ethers. There are included basic catalysts such as sodium methylate, sodium hydroxide, potassium hydroxide, lithium carbonate and the like acidic catalysts such as boron trifluoride and the like; amine catalysts such as trimethylamine, triethylamine and the like.

Furthermore, the compound having a structure of the formula ① wherein Y is a polymerizable functional group may be obtained by a method in which an active hydrogen compound is reacted with glycidyl ethers to obtain a polyether compound as described above and then, if necessary, a polymerizable functional group is introduced to the end of the main chain of the polyether compound.

Among the polymerizable functional groups, there are included an alkenyl such as vinyl and the like; an group having an unsaturated bond such as acryloyl, methacryloyl and the like; an group having straight chain and cyclic portion containing SI and the like. These groups are introduced into the molecule by reacting the above polyether compound with a compound having the polymerizable functional group.

As the compound having the polymerizable functional group, there are exemplified the following compounds; such as compounds having at least on carboxyl group and at least one unsaturated bond in the molecule, e.g., acrylic acid, methacrylic acid, cinnamic acid, maleic acid, fumaric acid, itaconic acid, polymental acid and the like; and/or anhydrides of the above compounds; e.g., maleic anhydride, itaconic anhydride and the like; and/or acid chlorides of the above compounds; glycidyls, e.g., allyl glycidyl ether, glycidyl methacrylate and the like; isocyanates, e.g., methacryloyl isocyanate and the like; the compounds containing Si, g, dichlorosilane, dimethyl vinylchlorosilan and the like. Thes compounds having the polymentable functional group may be used solely or in combination to produce the polymerizable compound having a structure of the formula ①.

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The compounds having a structure of the formula (1) thus prepared may be used solely or in combination. Howev r. it is important that the compound having an average molecular weight of 1,000 to 20,000 is used in any event. When the average molecular weight is less than 1,000, the film-formability of the product becomes poor, and when the average molecular weight is more than 20,000, the physical

editions in susproperty of the film becomes bad, produce the case is a supported to the number of active and the corresponds to the number of active hydrogen groups in the active hydrogen compound used as the starting material and is an integer of 1 to

12. The crosslinking reaction of the compound having a structure of the formula ① wherein Y is a hydrogen atom may be carried out by using as a crosslinking agent at least one polyisocyanate compound such as 2,4-tolylene diisocyanate (2,4-TDI); 2,6-tolylene diisocyanate (2,6-TDI), 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI), isophorone diisocyanate, triphenylmethane triisocyanate, tris(isocyanatephenyl) thiophosphate, lysine ester triisocyanate, 1,8-diisocyanate-4-isocyanatemethyloctane, 1,6,11-undecane triisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, biuret-bonded HMDI, isocyanurate-bonded HMDI, an adduct of trimethylolpropane with 3 moles of TDI and the like.

The used amount of the crosslinking agent is preferably selected so that the number of isocyanate group in the crosslinking agent becomes 1 to 1.5 times of the number of hydroxyl group in the compound thaving a structrue of the formula On 15 m 155 m tests

Further, to complete rapidly the crosslinking reaction, it is preferred to use a catalyst. Among the catalysts, there are included such as organic metal catalysts, e.g.-, dibutyltin dilaurate (DBTDL), dibutyltin diacetate (DBTA), salt of phenyl mercury propionic acid, lead octenate and the like; amine catalysts, e.g., triethylenediamine, N.N dimethylpiperazine, N-methylmorpholine, tetramethyl guanidine, triethylamine and

Next, the crosslinking reaction of the compound having a structure of the formula ① wherein Y is a polymerizable functional group may be different depending on the nature of the structure and the type of the polymerizable functional group. However, the reaction may be carried out with the use of available 6 the 10 commeans for film-forming such as heat, light and electronic ray. If necessary, a polymerization initiator and/or a

ones to the evsensitizer may be added in the reaction system. The top of the constitution of the crosslinking reaction, there are exemplified the following compounds; such as inorganic-ion salts containing at least one metal element selected from the group consisting of Li, Na, K, Cs, Ag, Cu and Mg, e.g., Lil, LiClo, LiClo, LiSCN, LiBF. LIASF6, LICF3SO3, LIC6F13SO3, LICF3CO2, LIHgl3, Nal, NaSCN, NaBr, KI, CSSCN, AgNO3, CuC12Mg(ClO4)-2 and the like; organic-ion salts, e.g., lithium stearyl-sulfate, sodium octylsulfate, lithium dodecylbenzenesulfate, sodium naphthalenesulfate; lithium dibutylnaphthalenesulfate, potassium octylnaphthalenesulfate, potassium dodecylnaphthalenesulfate and the like.

The added mol ratio of the soluble electrolyte salt to the number of oxyethylene unit (hereinafter referred to as "EO") comprised in the above organic polymer is preferably 0.0001 = 5.0 (mol/EO). When the soluble electrolyte salt is added in too high ratio, excess of the soluble electrolyte salt such as inorganic-ion salt does not dissociate but merely is present as a mixture and resultantly the ionic Was to appropriately is adversely lowered. S. O. S. A. S. A.

The soluble electrolyte salts may be used solely or in combination. The method for doping is also not n in : v sen restricted but it is generally convenient that the salts are dissolved in an organic solvent such as methyl ethyl ketone (MEK), tetrahydrofuran (THF) and the like and mixed with the organic polymers uniformly and then the organic solvent is removed under reduced pressure

According to the invention, as a glycidyl ether is used in the constitution of the main chain of the organic polymer, the structure of the organic polymer is made to be amorphous completely and the crystallization temperature is lowered by the presence of the side chain similar to the main-chain. When a lithium salt is used as the soluble electrolyte salt, the movement of the lithium cation is made easy and lithium-ion conductivity in a temperature range not higher than room temperature is remarkably improved.

When an active hydrogen compound is crosslinked with a crosslinking agent such as polyisocyanate and the like, a film superior in both of curability and adhesion to the electrode can be obtained and thus an ion-conductive polymer electrolyte excellent in practical utility can b provided. On the other hand, when a compound having a polymerizable functional group in the molecular is used, no crosslinking agent is required to carry out the crosslinking reaction. Accordingly it is safe and it can shorten the crosslinking

Furthermore, according to the invention, the organic polymer can be made more amorphous to give various forms of the product and accordingly it is very useful. 3774 383 85W 28 4 8

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Brief Description of the Drawing

The single figure of the drawing is a graph illustrating the relationshop between the temperature and the s ion conductivity of the ion-conductive polymer electolytes obtained in the after-mentioned Example Example 2 and Comparative Example 1.

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50 grown below 1 mol of glycerol (92 g) was reacted with 22 mol of methyldiethylene glycologlycidyle ether (3,874 g) so grown to dend mot of glycerol (92 g) was reacted with 22 more of the control o

ensures refer to entrance of 0.15 mol of potassium hydroxide (8.4 g) for 6 hours at 120 for with a consecutive-PUBLISHED TO THE TOTAL BEING introducing method and the reaction was further continued at the same temperature for 2 hours. Then the OF 1327 neith product was purified to obtain 3,570 g of an organic comound having an average molecular weight of 4,900 considered by hydroxide value) and a structure of the formula in which stocked on the common section of the control of the con

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R:-CH₃

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te custo a company in massification as a son the conm : 22. 3.6 g of thus obtained organic compound, 0.12 g of LICIO4, the 1.5 equivalent weight of tolylene disocyanate to the above organic compound and 0.01rg of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60 °C under atmospheric pressure in a stream of nitrogen gas. Then the solution was heat-treated for 8 hours at 80 °C in vacuum degree of below 1 x 10 73 Torr to remove methyl ethyl ketone, resultantly an ionconductive polymer electrolyte having a thickness of 50 µm was obtained. (0) Dictions

His Tourist of the command templates, explicit encouragement to the purely command by An ion-conductive polymer electrolyte was obtained in the same manner as in Exampl 1 except that the usage amount of LiClO; was changed to 0.06:g.o.h. have the reference of the second in with earlied for your appropriate thelepus styling to his order of the earlies

কাল হ'ব হ'ব জন্মি কালে কোনে হ'ব হ'ব হ'ব সংক্ৰম হ'ব সংক্ৰম হ'ব সংক্ৰম হ'ব THE RESERVE OF THE PROPERTY OF ্ৰ নিৰ্দেশ কোনালৈ হাট প্ৰতি হাতৃত্বহাহতি শতিবাৰে সভাৱত ইচিছে প্ৰতিব

Example 31.1 In the line of the process persons of the contract of

30 g of ethylene glycol was reacted with 1,910 g of n-butyl-triethylene glycol glycidyl ther represented by the following formula-

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CH2-CH-CH2-0- (CH2-CH2-0) 3-C4H9 on can his extensionally increases your pittern to be justiced from the business of the

in the presence of 6.8 g of potassium hydroxide for 6 hours at 120 C with a consecutive introducing method and further the reaction was continued at the same temperature for 2 hours. The produce was purified to obtain 2,094 g of an organic compound having an average molecular weight of 3,950 and a structure of the formula (1) in which

which is the Collins of the spiral and the CH20 to be a to make the set of the CH20 to be a to make the set of the CH20 to be a to make the set of the CH20 to be a to make the set of the CH20 to be a to make the set of the CH20 to be a to make the set of the CH20 to be a to make the set of the characters and the characters are the characters and the characters are the characters and the characters are the ch

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n : 3

m: 15

3.8 g of thus obtained organic compound, 0.12 g of LiClO4, the 0.7 equivalent weight of biuret-bonded HMDI to the above organic compound and 0.01 g of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60 °C under atmospheric pressure in a stream of hitrogen gas. Then the solution was heat-treated for 8 hours at 80 C in vacuum degree of below 1 x 10 = Form to remove methyl ethyl ketone, resultantly an ionconductive polymer electrolyte having a thickness of 50 μm was obtained. A ready O CE is register of the victures degree of caste will and the forton in the made

recture of the formula (D) in whiler

Z. - N -: CP3-CH3- N)--

Example 4

20 g of ethylenediamine was reacted with 2,650 g of phenylhexaethylene glycol glycidyl ether represented by the following formula 18 f. f. 18 " Letoss' sew A mississis to g 35

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CH2—CH-CH2-0-(CH2-CH2-0) 6-

in the presence of 9.4 g of potassium hydroxide for 6 hours at 120°C with a consecutive-introducing method and the leartion was further continued at the same temperature for 2 hours. Then the produce was purified to obtain 2,360 a of an organic compound having an average molecular weight of 7,870 and a has 017901 structure of the formula Din which and agreed business. The body of the policy sufficiency

$$Z : \mathsf{CH}_{\mathsf{Z}} - \mathsf{N} < \mathsf{CH}_{\mathsf{Z}} - \mathsf$$

3.6 g of thus obtained organic compound, 0.12 g of LiClO4, the 1.5 equivalent weight of MDI to the above organic compound and 0.01 g of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60 C under atmospheric pressure in a stream of nitrogen gas. Then the solution was heat-treated for 8 hours at 80°C in vacuum degree of below 1 xe10 m form to remove methyl ethyl ketone, resultantly an ion-conductive polymer electrolyte having a thickness of 50 jum-was obtained.

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Example 5

30 g of pentaethylenehexamine was reacted with 1,920 g of methyltriethylene glycol glycidyl ether represented by the following formula.

in the presence of 6.9 g of potassium hydroxide for 6 hours at 120 °C with a consecutive-introducing method and the reaction was further continued at the same temperature for 2 hours. Then the product was purified to obtain 1,598 g of an organic compound having an average molecular weight of 13,660 and a structure of the formula (1) in which

The content of 1.30 is a serior of the compound of 1.5 g of LICIO. The 1.5 equivalent weight of tolylene disocyanate to the above organic compound and 0.01 q of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60°C under atmospheric pressure in a stream of nitrogen gas. Then the solution was heat-treated for 8 hours at 80 °C in vacuum degree of below 1 x 10 -3 Torr to remove methyl ethyl ketone, resultantly an ionconductive polymer electrolyte having a thickness of 50 µm was obtained.

Applicant. Example 62 Vot a well rejected to 10 will fig. 12 to passes where each expense when

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20 g of Bisphenol A was reacted with 1,140 g of methyldodecaethylene glycol glycidyl ether represented by the following formula

in the presence of 4.19 g of potassium hydroxide for 6 hours at 120 C with a consecutive-introducing method and the reaction was further continued at the same temperature for 2 hours. Then the product was purified to obtain 1,060 g of an organic compound having an average molecular weight of 12,710 and a structure of the formula (1) in which

R:-CH₃

n : 12

grammer injuries arganic compound out 2 g of little-Daume 3.6 g of thus obtained organic compound; 0.12 g of LiClO., the 0.7 equival nt weight of biuret-bonded HMDI to the above organic compound and 0.01 g of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60 *C under atmospheric pressure in a stream of nitrogen gas. Then the solution was heat-treated for 8 hours at 80 °C in vacuum degree of below 1 x 10 Ta Torr to remove methyl ethyl k tone, resultantly an ionconductive polymer electrolyte having a thickness of 50 µm was obtained.

Example 7

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20 g of monoethanolamine was reacted with 1,630 g of phenyldiethylene glycol glycidyl ether represented by the following formula

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TO KOY ! FTO LES in the presence of 5.8 g of potassium hydroxide for 6 hours at 120 °C with a consecutive introducing method and the reaction was further continued at the same temperature for 2 hours. Then the produce was purified to obtain 1,430 g of an organic compound having an average molecular weight of 4,830 and a structure of the formula (1) in which 1 (1989 0.0) I stamped selling mod

Z: ÇHz-CHz-0-

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3.6 g of thus obtained organic compound, 0.12 g of LiClO4, the 1.5 equivalent weight of tolylene diisicyanate to the above organic compound and 0.01 g of dibutyltin dilaurate were dissolved in 3 ml of methyl ethyl ketone and then the mixture was poured into a flat vessel and allowed to stand for 30 minutes at 60 °C under atmospheric pressure in a stream of nitrogen gas. Then the solution was heat-treated for 8 hours at 80 °C in vacuum degree of below 1 x 10 3 Torrito remove methyl ethyl ketone, resultantly an ionconductive polymer electrolyte having a thickness of 50 um was obtained.

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To the 35 Comparative Example 1 An jon-conductive polymer electrolyte was robtained in the same manner as in Example 1 except that 3.6 g of a random polyether (ethylene oxide/propylene oxide = 8/2) having an average molecular weight of 3,000 was used instead of 3.6 g of the organic polymer used in Example 1 and 0.2 g of LiClO. was used instead of 0.12 g of LiClO4. the basis consider a struct that is the rector. mathematical terminal may posterior enterior and englines for the parties of the control of the total parties and the after each approximate of the control of

est formed in the bot energy specification of the second constants of the second on an analysis of the second conductivity test.

Each of the ion-conductive polymer electrolytes obtained in Examples 1 to 7 and Comparative Example 2 was interposed between platinum electrodes and the alternating current impedance between electrodes was measured and the complex impedance was analyzed. The results are shown in following Table 1.

Further, the same results are shown in the drawing with respect to Examples 1 and 2, and Comparative Example 1. -0:8J

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Table 1

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2.15 - 100		onic conductivit	y (S/cm)
	20 C	0. C	-20 °C
Example 1	1.8 x 10 ⁻⁵	√3.5, x 10 ⁻⁶	2.6 x 10 ⁻⁷
2	1.3 x 10 ⁻⁵	2,8 x 10 ⁻⁶	2.0 x 10 ⁻⁷
3	1.0 x 10 ⁻⁵	2.2 x 10 ^{−6}	1.8 x 10 ⁻⁷
4	2.8 x 10 ⁻⁵	4.2 x 10 ⁻⁶	3.1×10^{-7}
# # D 1981 # 25:00. 9 5.3	21 x 10 5	" 3.8 x 10 ^{—6}	.3 6:2:9 x 10 ⁻⁷
Shall employment of 6	2.5 x 10 ⁻⁵	4.0 x 10-6	% 63.0 x:10 ⁻⁷
Cry aforese un outy 2 i	1.6 x 10-5	-3.6 x 10 €	2.6 x 10 ⁻⁷
Comparative Example 1	3.0 x 10 ⁻⁶	2:3 x 10 ⁻⁷	below 1.0 x 10 ⁻⁸

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From the result decribed in Table 1, the lithium-ion conductivity according to the present invention is superior to that in Comparative Example 1 and its superiority becomes remarkable with lowering temperature. And it is obvious that the higher lithium-ion conductivity is shown even if the doping amount of the soluble salt of electrolyte such as LiClO₄ and the like is small. The ion-conductive polymer electrolyte according to the present invention has high practical superiority in this respect.

Example 8

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in the presence of a catalyst (2 g of potassium hydroxide). The product was purified with desalting to obtain 876 g of polyether having an average molecular weight of 4,890 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of acrylic acid to the hydroxide number of the polyether were added to benzene the used amount of which is equivalent with that of the acrylic acid. The mixture was reacted by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90° C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly, the formation of a terminal acryliated polyether having a molecular weight of 5,053 and a structure of the formula (1), in which

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CH20
CH20-

and the first of the transfer temperatures of the entire colors.

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Y:- C CH = CH₂
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R:-CH_{3.} k:3,

was confirmed by measuring the bromine value and the saponification value.

3.6 g of thus obtained terminal-acrylated polyether, 0.13 g of LiSCN (0.025 mol/EO) and 1 % of a

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polymerization initiator (2,2'-azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl keton and allowed nisch vir politikto stand for 1 hour at 80 °C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 -3 Torr to remove was a methyl ethyl ketone, and resultantly an ion-conductive polymer electrolyte having a thickness of 48 µm was tal munda e dibtained. Dispositios fors form town contined all other to house as property assign, or or other e

solution of the recording confined by the supplied of the second water and one and content. Lib xnrbyd, ma **Example 9**hilios propaga po ithiw becambosh (Law (Lot) be eth Libbosh is the next concerned a

Security of the electric from the content of the second of the content of the con following formula of 15,412 and a relation were treetly (D. In with

in the presence of a catalyst (2.7 g of potassium hydroxide). The product was purified with desalting to obtain 954 g of a polyether having an average molecular weight of 11,760 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of methacrylic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that of the methacrylic acid. The mixture was reacted by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly, the formation of a terminal-acrylated polyether having an average πolecular weight of 12,173, and a structure of the formula ①, in which

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m:9

n:3 R:-CH3

k:6,

was confirmed by measuring the bromine value and the saponification value.

3.6 g of thus obtained terminal-methacrylated polyether, 0.12 g of LiClO₄ (0.01 mol/EO) and 1 % of a polymerization initiator (2,2 -azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl ketone and allowed to stand for 1 hour at 80 C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 13 Torr to remove methyl ethyl ketone, and resultantly an ion-conductive polymer electrolyte having a thickness of 48 µm was to were thin. Both obtained, the total to be to distinguished at notice to the order of the control of the control of the principal of the first of the successful of the control of the c

and the end of the end of the rest continued by measuring the effluent amount of water to distribute to the The complete to the second of the positiveness as notific and modeson, the contract and is retained intelligent authorities accepted participal at femilies of the ac-

15 g of glycerol was reacted with 2,650 g of methylh xaethylen glycol glycidyl ether represented by the following formula . The means of the frimula in solution of the frimula in solutions and an arms of the following formula in the following for

in the presence of a catalyst (5 g of potassium hydroxide). The product was purified with desalting to obtain 2,160 g of a polyether having an average molecular weight of 15,260 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of acrylic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that the acrylic acid. The mixture was reacted by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuing the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly; the formation of a terminal-acrylated polyether having a molecular weight of 15,422 and a structure of the formula ①, in which

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The politic set up to the Complete to whight of medicarylic and the Medicary with number of the observation of the content of the methacrylic subservation with the desirable methacrylic subservation was recognized to the methacrylic subservation with the content of the reaction, the pollution was negligible. When the content of the reaction, the pollution was negligible, with the content of the reaction, the pollution was negligible with the content of the reaction, the pollution was negligible.

was confirmed by measuring the promine value and the saponification value. 3.6 g of the terminal acrylate polyether obtained above, 0.14 g of LCIO. (0.022 meVEO) and 1 % of polymerization initiator (2.2-azoisobutylonitrile) were dissolved in 3 mil of methyl ethyl ketone and allowed to stand for one hour at 80 °C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1, x 10 ⁻³ Torr to remove methyl ethyl ketone, resultantly an ion-conductive polymer electlyte having a thickness of 45 µm was obtained.

Example 11

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20 g of monoethanolamine was reacted with 1,630 g of phenyldiethylene glycol glycidyl ether represented by the following formula

CH2—CH-CH2-0- (CH2-CH2-0) 2-

in the presence of a catalyst (5.8 g of potassium hydroxide). Then the product was purified with desalting to obtain 1,430 g of a polyether having an average molecular weight of 4,830 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of acrylic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that of the acrylic acid. The mixtur was reacted by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate, and then benzene was removed under r düced pressure. Resultantly, the formation of a terminal-acrylated polyether having an average molecular weight of 4,990 and a structure of the formula ①, in which

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was confirmed by measuring the bromine value and the saponification value.

3.6 g of thus obtained terminal-acrylated polyether, 0.11 g of NaClOs (0.015 mol/EO) and 1 % of a polymerization initiator (2,2'-azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl ketone and allowed to stand for one hour at 80°C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 $^{-3}$ Torr to remove methyl ethyl ketone and resultantly an ion-conductive polymer electrolyte having a thickness of 45µm was ten in 12 to 12

as sur to entrum entered that we will writing to other their upening one increase entered the state. will see a second control of the second seco this grioti Example 12' That 08 to an except all a bas protitive to bloom that pullable ye become

ाउन्हरीका है है है है जिस्सा सबह वस्तुमी सालवा पुर सामकाडा तीर होसियल बरायधार को अवस्ति के जिल्ला मेर हैं है ह glycidyl ether 20 g of Bisphenol A was reacted with 11,140 g of nethyldodecaethylene glycol ears research represented by the following formula subscribe betauties is also content to my part

in the presence of a catalyst (4.2 g of potassium hydroxide) and the product was purified with desalting to obtain 1,060 g of a polyether having a molecular weight of 12,710 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of p-vinylbenzoic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that the p-vinylbenzoic acid. The mixture was reacted by adding 0.01 % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly, the formation of a polyether having p-vinylbenzoate bond at terminal and having a mulecular weight of 12,970 and a structure of the formula(1), in which

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R:-CH3 k: 2,

was confirmed by measuring the bromine value and the saponification value.

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3.6 g of thus obtained polyether having p-vinylbenzoate bond, 0.10 g of NaSCN (0.015 mol/EO) and 1 % of a polymerization initiator (2.2 -azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl ketone and allowed to stand for one hour at 80 °C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 -3 Torr to remove methyl ethyl ketone and resultantly an ion-conductive polymer electrolyte having a thickness of 42µm was obtained.

Example 13

20 g of ethylenediamine was reacted with 2,650 g of phenylhexaethylene glycol glycidyl ether represented by the following formula, 💲

action of the content everses on the fig. of a complete element into the substraints of the element of the second of the elements of

20 in the presence of a catalyst (9.4 g of potassium hydroxide). The product was purified with desalting to obtain 2,360 g of a polyether having a molecular weight of 7,870 (calculated by hydrexide value).

The polyether and the 1.1 equivalent weith of acrylic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that of the acrylic acid. The mixture was reacted by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Aesultantly, the formation of the terminal-acrylated polyether having a molecular weight of 8,084 and a structure of the formula O in which

Z : CH_z-N< CH_z-N< अविकास के किया है। अने कार की एक काम के इन्लोकी लोगों की अन्यान के हैं जिस्से के स्वास्त्र के हैं जिस के स्वास

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was confirmed by measuring the bromine value and the saponification value.

3.6 g of thus obtained terminal acrylate polyether, 0.09 g of LISCN (0.020 mol/EO) and 1 % of a polymerization initiator (2,2 azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl keton and allowed to stand for on hour at 80°C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 -3 Torr to remove methyl ethyl ketone, and resultantly an ion-conductive polymer electrolyt having a thickness of 41 µm was obtained.

30 g of ethylene glycol was reacted with 2.650 g of n-butyl triethylene glycol glycidyl ether represented by the following formula

in the presence of a catalyst (6.8 g of potassium hydroxide). The product was purified with desalting to obtain 2,094 g of a polyether having an average molecular weight of 3,950 (calculated by hydroxide value). The polyether and the 1.1 equivalent weight of p-vinylbenzoic acid to the hydroxide number of the polyether were added to benzene the used amount of which is identical with that of the p-vinylbenzoic acid ocitals; and the mixture was reacted by adding 0.01 mol % of suffuric acid at a temperature of 80 to 90 °C with evames as sintroducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly, the formation of a polyether having pvinylbenzoate bond at terminal and having an average molecular weight of 4,213 and a structure of the formula (1), in which

Z: -O-CH2-CH2-O-

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As a structure of the structure of the property of the saponification value to provide the saponification value to provide the saponification value to provide the provided and the saponification value to provided and the saponificati bergeet asyr enum 3.6 g of thus obtained polyether having p-vinylbenzoate bond at terminal, 0.10 g of LiCIO. (0.015 polymerization initiator (2,2 azoisobutylonitrile) were dissolved in 3 mi of methyl eithyl ketone and allowed to stand for one hour at 80 °C in a stream of nitrogen gas under atmospheric pressure. Then the solution was neat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 -3 Torn to remove methyl eithyl ketone, and resultantly an ion-conductive polymer electrolyte Endon a sew below, so having a thickness of 50 mm was obtained to superpresent at a think terms against a control of the having a thickness of 50 mm was obtained to substruct at the having a thickness of 50 mm was obtained.

Example 15

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30 g of pentaethylenehexamine was reacted with 1,920 g of methyltriethylene glycol glycidyl ether represented by the following formula

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The product was purified with desalting to say the presence of a catalyst (6.9 g of potassium hydroxide). The product was purified with desalting to obtain 1,598 g of a polyether having an average molecular weight of 13,660 (calculated by hydroxide value).

The polyether and the 1.1 equivalent weight of methacrylic acid to she hydroxide number of the polyether were added to benzene the used amount of which is identical with that the p-vinylbenzoic acid. The mixture was reacted by adding 0.01 mol % of sulfuric acid at a temperatur of 80 to 90°C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water

and the acid value, and the reaction, the solution was neutralized with an aqueous solution of sodium and then b nzene was removed under reduced pressure. Resultantly, the formation of the terminal-methacrylated polyether

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having an average molecular weight of 14,200 and a structure of the formula 1, in which Z:- N -(CH2-CH2-N) 5

 $Y:-\overset{\circ}{C}C(CH_3)=CH_2$

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k 8) VI USBILLIAN) 085,8 to tradew and the saponification value. A 100 S was confirmed by measuring the bromine value and the saponification value.

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10 16 3.6 g of thus obtained terminal-methacrylated polyether, 0.23 g of LICIO. (0.025 mol/EO) and 1 % of a pólymerization initiator (2.2 -azoisobuty)onitrile) were dissolved in 3 ml of methyl ethyl ketone and allowed to stand for arhour at 80 nC in a stream of nitrogen gas under atmospheric pressure. Then the solution was to remove the streated for Schours, at the same temperature in vacuum degree of below 10x110x3 Torr to remove methyl ethyl ketone, and resultantly an ion-conductive polymer electrolyte having a thickness of 45 µm was and a broad to decrease the administry the formation of abolities of the

Example 16

20 g of ethylene glycol was reacted with 6,250 g of methyl glycidyl ether represented by the following 20 formula

in the presence of a catalyst (10 g of potassium hydroxide). The product was purified with desalting to obtain 5,970 g of a polyether having an average molecular weight of 19,020 (calculated by hydroxide value).

The polyether and the 1/1 equivalent weight of acrylic acid to the hydroxide number of the polyether The polyether and the interpolyether and the by adding 0.01 mol % of sulfuric acid at a temperature of 80 to 90 °C with introducing air. The completion of the reaction was confirmed by measuring the effluent amount of water and the acid value. After completion of the reaction, the solution was neutralized with an aqueous solution of sodium hydroxide. The product was washed with a saturated aqueous solution of sodium sulfate and then benzene was removed under reduced pressure. Resultantly, the formation of a terminal-acrylated polyether having an average molecular weight of 19, 160 and a structure of the formula (1), in which Z: -O-CH2-CH2-O-

Y:- CH = CH2

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n:0

R: -CH₃

k: 2, was confirmed by measuring the bromine value and the saponification value.

3.6 g of thus obtained terminal-acrylated polyether, 0.13 g of LiClO4 (0.015 mol/EO) and 1 % of a polymerization initiator (2.2'-azoisobutylonitrile) were dissolved in 3 ml of methyl ethyl ketone and allowed to stand for 1 hour at 80°C in a stream of nitrogen gas under atmospheric pressure. Then the solution was heat-treated for 8 hours at the same temperature in vacuum degree of below 1 x 10 -3 Torr to remove methyl ethyl ketone, and resultantly an ion-conductive polymer electrolyte having a thickness of 42 μm was methyl ethyl ketone, and resultations and especies of garvia and any and a property obtained. The order of the mean is of piers the larger of the larger of

the second black of the contract of the second because the second because the second of the second black o s Comparative Example 2 Version of the property of the propert

An ion-conductive polymer electrolyte was obtained in the same manner as in Example 1 except that a random ether (ethylene oxide/propylene oxide = 8/2) having an average molecular weight of 3,000 was used instead of the polyether having an average molecular weight of 4,890 to produce the terminalacrylated polyether, and 0.20 g of LiClO, was used instead of 0.13 g of LiSCN.

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[Litium-ion conductivity test]

Each of the ion-conductive polymer electrolytes obtained in Example 8 to 16 and Comparative Example 2 was interposed between platinum electrodes and the alternating current impedance between electrodes was measured and the complex impedance was analyzed. The results are shown in following Table 2. Table 16 griffished affect and and accompanies of great and great at the printing of affect and accompanies of the printing of affect and accompanies of the printing of affect and accompanies of the printing of a feet and accompanies of the printing of t

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toths of Market (167 - 170 strongwest	Example 8	1.1 x 10 ⁻⁵	2.8 x 10=6 2.8 x 10=6	.೧೬೬೧ ೧೯2.1:x410T/ ದೆಚಳಿತ ೧ ೮.0 x 10 T/ನಿರ್ಗತ	
15	Example 10 Example 11	2.1 x 10 ⁻⁵ 2.2 x 10 ⁻⁵	2.5 x 10 ⁻⁶ 3.8 x 10 ⁻⁶	2.8 x 10 ⁻⁷ : , 2.7 x 10 ⁻⁷ 2.4 x 10 ⁻⁷	
Ťn	Example 12 Example 13	2.1 x 10 ⁻⁵ 1.8 x 10 ⁻⁵ 1.2 x 10 ⁻⁵	3.7 x 10 ⁻⁶ 3.0 x 10 ⁻⁶ 2.3 x 10 ⁻⁶	1.9 x 10 ⁻⁷ 1.8 x 10 ⁻⁷	
20	Example 14 Example 15 Example 16	2.1 x 10 ⁻⁵ 1.0 x 10 ⁻⁵	3.7 x 10 ⁻⁶ 2.3 x 10 ⁻⁶	3.0 x 10 ⁻⁷ 1.6 x 10 ⁻⁷	
•	Comparative Example 2	2.5 x 10 ⁻⁶	2.1 x 10 ⁻⁷	below 1.0 x 10 ⁻⁸	

From the result decribed in Table 2, it is found that the ionic conductivity of the ion-conductive polymer electrolyte according to the present invention is very excellent and its superiority becomes remarkable with lowering temperature and higher lithium-ion conductivity can be obtained by use of small doping amounts of the soluble salt of electrolyte having such as LiClO4 and the like.

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[Effects of the Invention]

The ion-conductive polymer electrolyte according to the present invention shows good ion-conductivity stably. And it can be taken in various forms since it can be made amorphous, therefore, it has very excellent practicality. Furthermore, the ion-conductive polymer electrolyte according to the present invention is superior in safetyness and can be available with good operation since it can be crosslinked without using a crosslinking agent.

Claims

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1. An ion-conductive polymer electrolyte comprising an organic polymer and a soluble electrolyte salt, characterized in that said organic polymer is obtained by crosslinking a compound having an average molecular weight of 1,000 to 20,000 and having a structure of the following formula(1);

in which Z is a residue of a compound having at least one active hydrogen, Y is a hydrogen atom or polymerization-reactive functional group, m is an integer of 1 to 250, n is 0 or an integer of 1 to 25, k is an integer of 1 to 12, R is an alkyl, alkenyl, aryl or alkylaryl group having 1 to 20 carbon atoms.

2. An ion-conductiv polymer electrolyte as defined in Claim 1, wherein said organic polymer is obtained by crosslinking with a crosslinking agent said compound having a structure of said formula (1) in which Y is a hydrogen atom.

3. An ion-conductiv polymer electrolyte as defined in Claim 2, wherein said crosslinking agent is an

isocyanate compound.

4. An ion-conductive polymer electrolyte as defined in Claim 1, wherein Y in said formula ① is a

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5. An ion-conductive polymer electrolyte as defined in anyone of Claims 1 to 4, wherein said soluble electrolyte salt is at least one selected from the group consisting of inorganic-ion salts containing at least one metal element selected from the group consisting of Li, Na, K, Cs, Ag, Cu and Mg, such as Lil, LiCl, LICIO4, LISCN, LIBF4, LIASF6, LICF3SO3, LIC6F13SO3, LICF3CO2, LIHgI3, Nal, NaSCN, NaBr, KI, CSSCN, AgNO3, CuC12Mg(CiO4)2; , and organic-ion salts such as lithium stearylsulfate, sodium octylsulfate, lithium dodecylbenzenesulfate, sodium naphthalenesulfate, lithium dibutylnaphthalenesulfate, potassium octylnaphthalenesulfate, potassium dodecylnaphthalenesulfate and the like.

6. An ion-conductive polymer electrolyte as defined in anyone of Claims 1 to 5, wherein the added amount of said soluble electrolyte salt to an oxyethylene unit in said organic polymer is 0.0001 - 5.0

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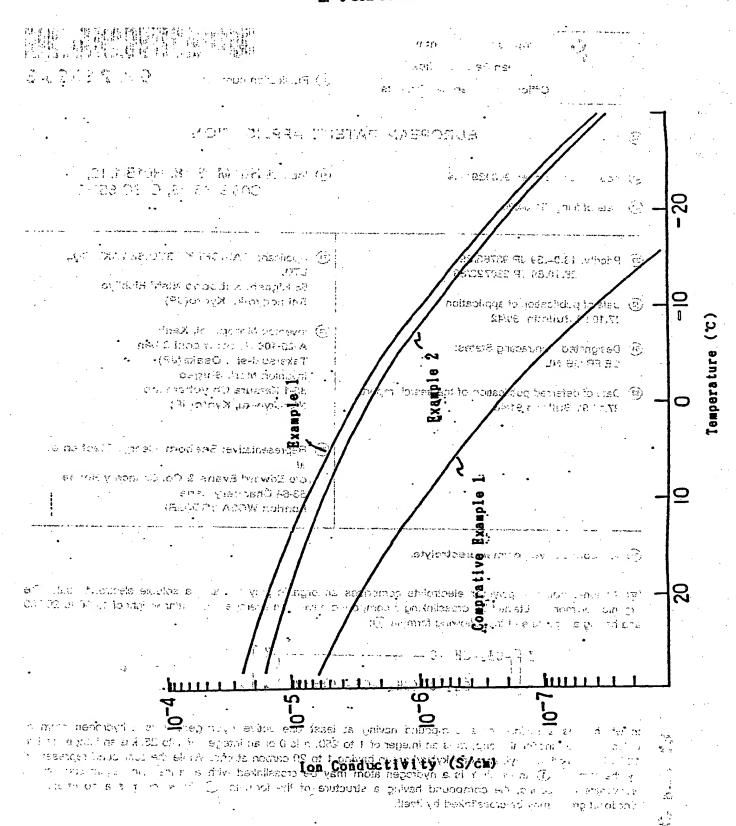
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EUROPEAN PATENT APPLICATION

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- 2 Date of filing: 11.04.90.

(s) Int. Cl.⁵. **H01M** 6/18, H01B 1/12, C08G 65/26, C08G 65/32

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- Date of publication of application: 17.10.90 Bulletin 90/42
- Designated Contracting States:
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- Applicant: DAI-ICHI KOGYO SEIYAKU CO., LTD. 55 Higashi-Kubocho Nishi-Hichijyo Shimogyo-ku Kyoto(JP)
- Inventor: Motogami, Kenji
 A-25-106 Noborimachi 2-ban
 Takatsuki-shi, Osaka(JP)
 Inventor: Mori, Shigeo
 35-1 Katsura Chiyoharacho
 Nishikyo-ku, Kyoto(JP)
- Representative: Seaborn, George Stephen et al c/o Edward Evans & Co. Chancery House 53-64 Chancery Lane London WC2A 1SD(GB)
- (3) Ion-conductive polymer electrolyte.
- An ion-conductive polymer electrolyte comprises an organic polymer and a soluble electrolyte salt. The organic polymer is obtained by crosslinking a compound having an average molecular weight of 1,000 to 20,000 and having a structure of the following formula ①;

in which Z is a residue of a compound having at least one active hydrogen, Y is a hydrogen atom or polymerizable functional group, m is an integer of 1 to 250, n is 0 or an integer of 1 to 25, k is an integer of 1 to 12, R is an alkyl, alkenyl, aryl or alkylaryl group having 1 to 20 carbon atoms. While the compound represented by the formula ① in which Y is a hydrogen atom may be crosslinked with a crosslinking agent such as an isocyanate compound, the compound having a structure of the formula ① in which Y is a polymerizable functional group may be crosslinked by itself.

EUROPEAN SEARCH REPORT រាល់ ភេឌភា ហៀ

Application Number \S

EP 90-30 3944

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